

CARBON NANOTUBE/SPACE DURABLE POLYMER NANOCOMPOSITE FILMS FOR ELECTROSTATIC CHARGE DISSIPATION

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ABSTRACT

Low solar absorptivity, space environmentally stable polymeric materials possessing sufficient electrical conductivity for electrostatic charge dissipation (ESD) are of interest for potential applications on spacecraft as thin film membranes on antennas, solar sails, large lightweight space optics, and second surface mirrors. One method of imparting electrical conductivity while maintaining low solar absorptivity is through the use of single wall carbon nanotubes (SWNTs). However, SWNTs are difficult to disperse. Several preparative methods were employed to disperse SWNTs into the polymer matrix. Several examples possessed electrical conductivity sufficient for ESD. The chemistry, physical, and mechanical properties of the nanocomposite films will be presented.

KEY WORDS: Carbon Nanotubes, High Temperature Polymers, Polyimides, ESD films

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1. INTRODUCTION

Space environmentally durable polymer films are needed in the development of large, deployable, ultra lightweight Gossamer spacecraft. One attribute of these films is the need to be fairly compliant so as to be folded into compact volumes suitable for conventional launch vehicles prior to launch. Upon achieving orbit, the film based structure would automatically deploy into structures that are many square meters in size (1). Besides being compliant, the materials must exhibit a unique combination of physical (e.g. optical and electrical) and mechanical properties. These properties include resistance to many environmental factors such as atomic oxygen, ultraviolet (UV) and vacuum (UV) radiation, etc.; all of which are dependent upon the intended orbit of the spacecraft. Some applications require low solar absorptivity and high thermal emissivity. Thus the focus of this work is to develop materials with an attractive overall combination of optical, electrical, thermal, and mechanical properties as well as environmental durability.

Aromatic polyimides are excellent materials for these applications due to their exceptional physical and mechanical properties as well as resistance to radiation. Low color (low solar absorptivity) and atomic oxygen resistance have been incorporated into polyimides by chemical modification of the polymer backbone and choice of the appropriate constituent monomers (2,3). However, the incorporation of sufficient electrical conductivity to mitigate electrostatic charge (ESC) build-up without degrading other desired properties has been difficult. Electrical conductivity in the material is needed due to the charged orbital environment. Insulating materials exposed to this environment become charged and as a consequence can behave like a capacitor. The problem with this effect is when the material discharges; it can occur in a single event that can cause damage to materials and electronics on the spacecraft. To mitigate ESC build-up, the surface resistance required is in the range of 10^6 to 10^{10} ohms/square.

One approach to incorporating sufficient electrical conductivity in an insulating polymer to mitigate ESC build-up without detrimentally affecting the optical properties of the material is through the incorporation of carbon nanotubes (CNTs). Discovered in 1991, CNTs were determined to exhibit exceptional mechanical and electrical properties and as a consequence much research has been ongoing to take advantage of these properties by their inclusion into polymeric systems. Carbon nanotubes have been prepared by processes such as arc discharge, laser ablation (LA), chemical vapor deposition, and high pressure carbon monoxide (HiPCO) as multiwalled (MWNT) and single walled (SWNT) varieties with the greatest property enhancements anticipated to come from the SWNTs (4,5). Due to the methodology employed in CNT synthesis, purification to remove residual catalysts and amorphous carbon has been proposed to introduce functionalities such as carboxylic acid and hydroxyl groups at the tube ends (6). It is known that improvements in certain mechanical and physical properties of a host polymer as compared to the virgin material can be obtained by the incorporation of

nanomaterials provided that the nanomaterials are uniformly dispersed throughout the matrix. This however has been difficult to achieve with CNTs due to the insolubility of the material and/or incompatibility with the host resin. Typically, CNTs tend to agglomerate as bundles in solvents and the host resin and if dispersed, reaggregate soon thereafter due to electrostatic attraction.

Methods of achieving good dispersion of SWNTs into LaRC™ CP2 and other space environmentally durable polymers such as TOR-NC have been reported (7, 8). One method involves the preparation of the polymer as the precursor amide acid in the presence of the CNTs with subsequent thermal conversion to the corresponding imide. Alternatively, the amide acid/SWNT mixture can be cyclized chemically in solution provided that the imide remains soluble. A second method involves the use of alkoxysilane terminated amide acid oligomers to disperse CNTs (9). Alkoxysilane containing materials, typically referred to as coupling agents, are known to aid in the adhesion of organic materials to inorganic substrates such as glasses, metals, and ceramics. The adhesion of the organic to inorganic is enhanced through the formation of covalent bonds between the coupling agent and the inorganic substrate. This bond is formed from condensation of silanol groups on the organic, generated in-situ from alkoxysilanes under acidic or basic hydrolysis conditions, with hydroxyl functionalities present on the inorganic. The amide acid is sufficiently acidic to initiate the hydrolysis reaction of the alkoxysilane to afford the corresponding silanol. Hydroxyl functionalities present on the inorganic may be naturally occurring or generated through chemical reactions on the inorganic surface. Upon thermal treatment, the hydroxy groups on the inorganic condense with silanol groups on the organic generating an oxane bond. This technology is typically employed to improve the hot-wet performance of composite and adhesives. The postulation was that the alkoxysilane functional ends on the oligomer, once hydrolyzed, would react with functionalities on the ends of the purified SWNTs. It was anticipated that this would aid in dispersion and compatibilization. The preparation and characterization of nanocomposite films derived from low color, space environmentally durable polymers [LaRC™ CP2 (3, 7) and TOR-NC (2, 8)] and SWNTs by both of these methods is described herein.

2. EXPERIMENTAL

2.1 Starting Materials The following chemicals were obtained from the indicated sources and used without further purification: aminophenyltrimethoxysilane (APTS, Gelest Inc., 90% meta, 10% para), 1,3-bis(3-aminophenoxy)benzene [APB, Mitsui Chemicals America, Inc. melting point (m.p.) 107-108.5 °C], [2,4-bis(3-aminophenoxy)phenyl]diphenylphosphine oxide (3-APPO, Sarchem Laboratories, Inc., m.p. 195-196 °C), dimethylformamide (DMF, Aldrich), and N,N-dimethylacetamide (DMAc, Aldrich). 4,4'-Hexafluoroisopropylidene diphthalic anhydride (6-FDA, Hoechst Celanese Inc., m.p. 241-243 °C) and 4,4'-oxydiphthalic anhydride (ODPA, Occidental Chemical Co., m.p. 229 °C) were sublimed prior to use. HiPCO SWNTs were

obtained from Tubes@Rice. The SWNTs were purified by soxhlet extraction with hydrochloric acid for ~24 hours. All other chemicals were used as-received without further purification.

2.2 In-situ Polymerization The following example is representative of the preparative method employed. A glass vial containing 0.0060 g of purified HiPCO SWNT and 10 mL of DMF was placed in an ultrasonic bath for periods ranging from 16 to 24 hours. A 100 mL three neck round bottom flask equipped with a mechanical stirrer, nitrogen gas inlet, and drying tube filled with calcium sulfate was charged with 3-APPO (3.6776 g, 7.467×10^{-3} mole) and DMF (5.0 mL). Once the diamine dissolved, the DMF/nanotube mixture was added and the resulting mixture stirred for 20 minutes at room temperature. ODA (2.3164 g, 7.467×10^{-3} mole) was then added along with additional DMF (8.2 mL) to give a solution with a concentration of 20% (w/w) solids and a nanotube concentration of 0.1% by weight. The mixture was stirred overnight at room temperature under a nitrogen atmosphere. The poly(amide acid) intermediate was chemically imidized by the addition of 2.31 g of acetic anhydride and 1.77 g of pyridine. The reaction mixture was stirred at room temperature overnight under a nitrogen atmosphere. The polyimide/SWNT mixture was precipitated in a blender containing deionized water, filtered, washed with excess water and dried in a vacuum oven at 150 °C overnight to afford a light gray, fibrous material.

2.3 Synthesis of Oligomers Alkoxysilane terminated amide acids (ASTAAs) were prepared by the reaction of 6-FDA with APB and end-capped with APTS at a 2.5% offset. The calculated number average molecular weight (\overline{M}_n) was ~27,700 g/mole. The oligomer was prepared by dissolving APB (6.3870 g, 0.0218 mol) and APTS (0.2390 g, 0.0011 mol) in DMAc (7 mL) at room temperature under nitrogen. The flask was then immersed in a water bath so as to regulate the temperature. Then 6-FDA (9.9547 g, 0.0224 mol) was added in one portion as a slurry in DMAc (10 mL) and rinsed in with 18 mL of DMAc to afford a solution with a solid content of ~33.5% (w/w). The reaction was stirred for ~24 hours at room temperature under nitrogen. An aliquot was removed to determine inherent viscosity. The solution was used as is or SWNTs were added as described in 2.4.

2.4 Blending of CNT and ASTAA The following example is representative of the preparative method employed. To a 100 mL round bottom flask equipped with a nitrogen inlet, mechanical stirrer, and drying tube filled with calcium sulfate was charged 11.06 g of an ASTAA solution (33.5% solids). HiPCO-SWNTs (0.0011 g) were placed in 3 mL of DMAc and the mixture was sonicated in a water bath at room temperature for ~2.5 hours. The suspended tubes were added to the stirred mixture of ASTAA at room temperature and rinsed in with 4.5 mL of DMAc to afford a solids content of ~20.4%. The SWNT concentration was ~0.03% by weight relative to the ASTAA. The mixture was stirred for ~16 hours under a nitrogen atmosphere at room temperature prior to film casting.

2.5 Films A solution, prepared from DMF or chloroform (20% solids w/w) from polyimide/SWNT mixtures prepared by the in-situ method described in 2.2, was cast onto plate glass and allowed to dry to a tack-free state in a dust-free chamber. The film on the glass plate was placed in a forced air oven at 100, 150, 175 and 225 °C for 1 hour each. The film was subsequently removed from the glass plate and characterized. The DMAc solutions of the ASTAAs (with and without HiPCO SWNTs as described in 2.3 and 2.4, respectively) were doctored onto clean, dry plate glass and dried to tack-free forms in a low humidity chamber at ambient temperature. The films on glass were cured in a forced air oven at 100, 200, and 300 °C for 1 hour each. The film was subsequently removed from the glass plate and characterized. Room temperature thin-film tensile properties were determined according to ASTM D882 using four specimens.

2.6 Characterization Inherent viscosities were obtained on 0.5% (w/v) amide acid solutions in DMAc at 25 °C. Differential scanning calorimetry (DSC) was conducted on a Shimadzu DSC-50 thermal analyzer. Melting point ranges (tangent of onset to melt and the endothermic peak) were determined by either DSC at a heating rate of 10 °C/min or visually on a Thomas-Hoover capillary melting point apparatus (uncorrected). Glass transition temperatures (T_g s) were determined at a heating rate of 20 °C/min and were taken as the inflection point of the ΔT vs temperature curve. UV/VIS spectra were obtained on thin films using a Perkin-Elmer Lambda 900 UV/VIS/NIR spectrometer. Solar absorptivities (α) were measured on an AZ Technology Model LPSR-300 spectrophotometer with measurements taken between 250 to 2800 nm with a vapor deposited aluminum on Kapton® film (1st surface mirror) as a reflective reference for air mass 0 per ASTM E903. An AZ Technology Temp 2000A infrared reflectometer was used to measure thermal emissivity (ϵ).

3. RESULTS AND DISCUSSION

3.1 Single Wall Carbon Nanotubes The objective of this work was to develop low color, optically transparent, space environmentally durable polymers with sufficient conductivity to mitigate static charge build-up. Previous work in our laboratory utilized SWNT produced by the laser ablation (LA) process (5-7). Elemental analysis of the purified tubes gave the following results: 75% C, 0.7% H, 0.2% Fe, 1.3% Co, and 1.2% Ni. The inorganic metals present were due to the catalyst employed in this process. The purification process entailed treatment with a mixture of sulfuric and nitric acids. The LA SWNT dispersed well in low color polyimides (LaRC™ CP2 and TOR-NC) with minimal effect upon the thermo-optical properties. However, mixed results were obtained for the surface resistivity measurements. In a majority of cases, no improvements in conductivity were obtained for the nanocomposite as compared to the virgin polymer. The reason for this is still unclear.

Work was then initiated using SWNT prepared by the high pressure carbon monoxide (HiPCO) process. Elemental analysis of purified tubes afforded the following results: 89% C, 0.5% H, and 1.8% Fe. For both SWNTs produced by the LA and HiPCO methods, oxygen content was not determined. It is postulated that the remaining mass balance is due to the presence of oxygen in the form of carbon-oxygen bonded species such as carboxylic acid and hydroxyl groups. Presumably these moieties occur at defect sites along the tube or perhaps at the tube ends. Analysis of the HiPCO prepared tubes by atomic force microscopy indicated that the tubes were roped into large bundles ~25 nm in diameter (Figure 1). Due to the large packing density the individual tubes could not be analyzed; however, the tubes appeared to be consistent with other HiPCO produced materials with the following dimensions: ~0.7 to 1.5 nm in diameter and in the micron range for length.

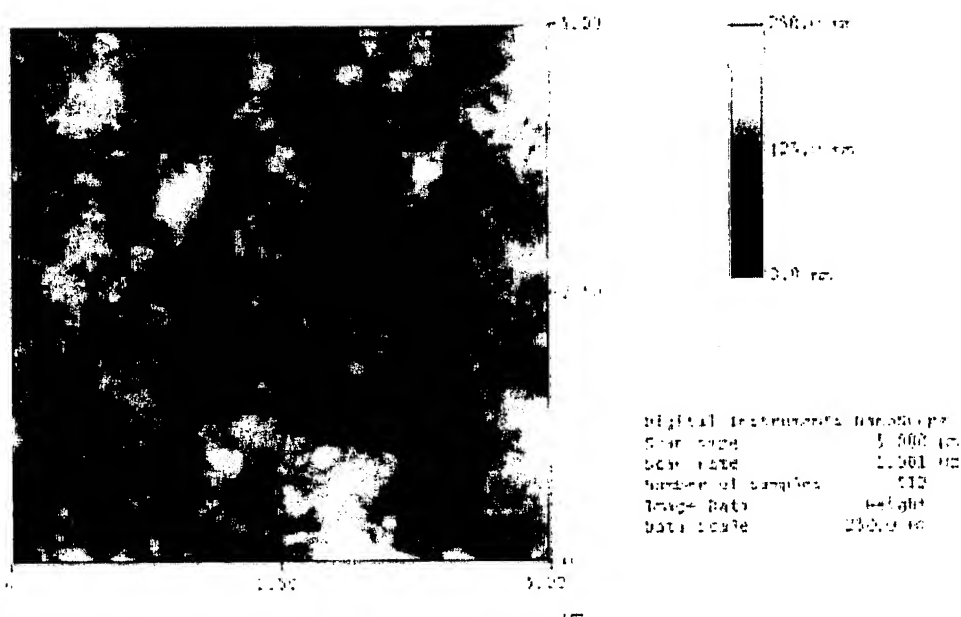


Figure 1. Atomic Force Microscopy Image of HiPCO SWNT.

3.2 Nanocomposites Prepared via In-Situ Polymerization Early on it was determined that the addition of SWNTs to an already prepared high molecular weight poly(amide acid) (or imide if soluble) solution and subjected to low shear mixing did not adequately disperse the SWNTs. Therefore the synthesis was conducted in the presence of the SWNT (7, 8). Prior work incorporated SWNT prepared from other processes such as LA with TOR-NC and LaRC™ CP2 (7, 8). The work described here is based upon TOR-NC and HiPCO SWNTs. The method involved initial sonication of the SWNTs in a polar aprotic solvent to adequately suspend the SWNTs. The diamine was then added to the suspension followed by the addition of the dianhydride (Figure 2). The mixture was allowed to stir under a nitrogen atmosphere at ambient

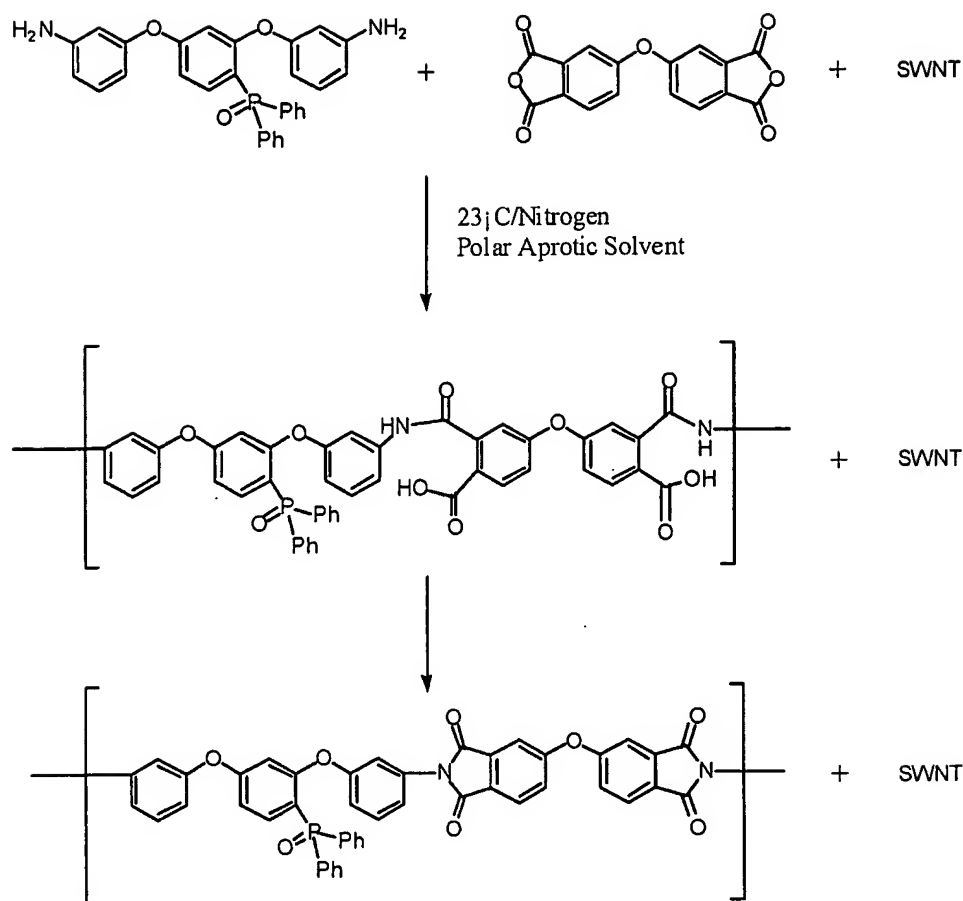


Figure 2. In-situ preparation of TOR-NC/SWNT nanocomposite.

temperature to afford a visually viscous solution and subsequently chemically imidized to the corresponding imide. Solutions with a 0.1 and 0.2% by weight concentration of SWNT were prepared. The polyimide/SWNT mixtures were isolated and redissolved in DMF prior to casting films. Films cast from the neat poly(amide acid) were darker in color and more brittle; presumably due to low molecular weight. Unoriented thin films were cast from the imide/SWNT compositions and air dried to 225 °C.

Physical and tensile properties of the polyimide/SWNT compositions are shown in Table 1. Properties for nanocomposite compositions prepared from LA SWNTs are included for comparison (8). The T_g s of the nanocomposite films prepared from the LA SWNT were markedly lower than those obtained for the HiPCO containing materials at the same

Table 1. TOR-NC Nanocomposite Characterization

SWNT Type	T _g ,	Room Temperature Tensile		Elong. @
(% incorporated)	°C	Strength, MPa	Modulus, GPa	Break, %
0	212	97	2.8	4.7
LA (0.1)	187	88	3.2	3.5
LA (0.2)	200	94	3.2	4.9
HiPCO (0.1)	209	101	2.7	4.2
HiPCO (0.2)	208	99	2.6	4.0

concentration. With both SWNT types, the T_g decreased relative to that of the neat material. The LA SWNT based nanocomposites exhibited a slight increase in tensile modulus, whereas no enhancement was observed with the HiPCO SWNTs. Tensile strength and % elongation remained relatively unaffected by the inclusion of either type of SWNT.

Optical transparency at 500 nm and thermo-optical properties were determined and reported in Table 2. In general, a 5-33% decrease in the % transmission at 500 nm was observed with a more marked decrease occurring with the HiPCO SWNTs. The effect of SWNT loading on the solar absorptivity (α) and thermal emissivity (ϵ) was of interest since these properties are important for some applications on Gossamer spacecraft. Solar absorptivity (α) pertains to the fraction of incoming solar energy that is absorbed by the film while the thermal emissivity (ϵ) is a measure of the films ability to radiate energy from the film surface. Typically a low colored film exhibits a low α . Care was taken to cast films of approximately the same thickness since this would effect the optical and thermo-optical properties. Film thickness ranged from 24 to 33 μm . A marked increase in the α was observed with the HiPCO SWNT nanocomposite films as compared to the neat material. As compared to films containing LA SWNT at the same concentration there was an $\sim 2.5\text{X}$ increase in α . The ϵ was slightly higher for the HiPCO SWNT containing films as compared to the LA SWNT films. Both SWNT materials exhibited an increase in ϵ as compared to the neat material.

Table 2. Optical and Thermo-optical Properties of TOR-NC Nanocomposites

SWNT Type	Film	Transmission	Solar	Thermal
(% incorporated)	Thickness, μm	@ 500 nm, %	absorptivity , α	Emissivity , ϵ
0	25	85	0.05	0.56
LA (0.1)	33	76	0.14	0.58
LA (0.2)	25	75	0.15	0.61
HiPCO (0.1)	24	81	0.36	0.65
HiPCO (0.2)	22	57	0.41	0.68

3.3 Nanocomposites Prepared from Alkoxysilane Terminated Amide Acids A second approach involved the use of oligomeric materials terminated with reactive endgroups. Initial work using this method involved the use of LA SWNTs (9). Trimethoxy silane endcapped LaRC™ CP2 amide acid (ASTAA) oligomers used to prepare HiPCO SWNT based nanocomposites presented here were prepared at a stoichiometric offset of 2.5%, which calculates to a \bar{M}_n of ~27,700 g/mol (Figure 3). The inherent viscosity of the oligomer was 0.88 dL/g. Precursor nanocomposite solutions were prepared by the addition of a sonicated suspension of SWNT in DMAc to a stirred solution of premade ASTAA to afford solutions with a 0.03, 0.05, and 0.08% by weight concentration of SWNT. The solutions were stirred for ~16 hours at ambient temperature prior to film casting. Once dried to a tack-free state, the films were cured to 300 °C in flowing air to effect imidization and condensation. Due to the acidic nature of the amide acid, no additional acid catalyst was required for the hydrolysis and condensation of the alkoxysilane endgroups. Nanocomposite physical and room temperature tensile properties are shown in Table 3. Material properties are included for a high molecular weight unendcapped (HMW) version of LaRC™ CP2 (3) as a comparison to the neat oligomeric

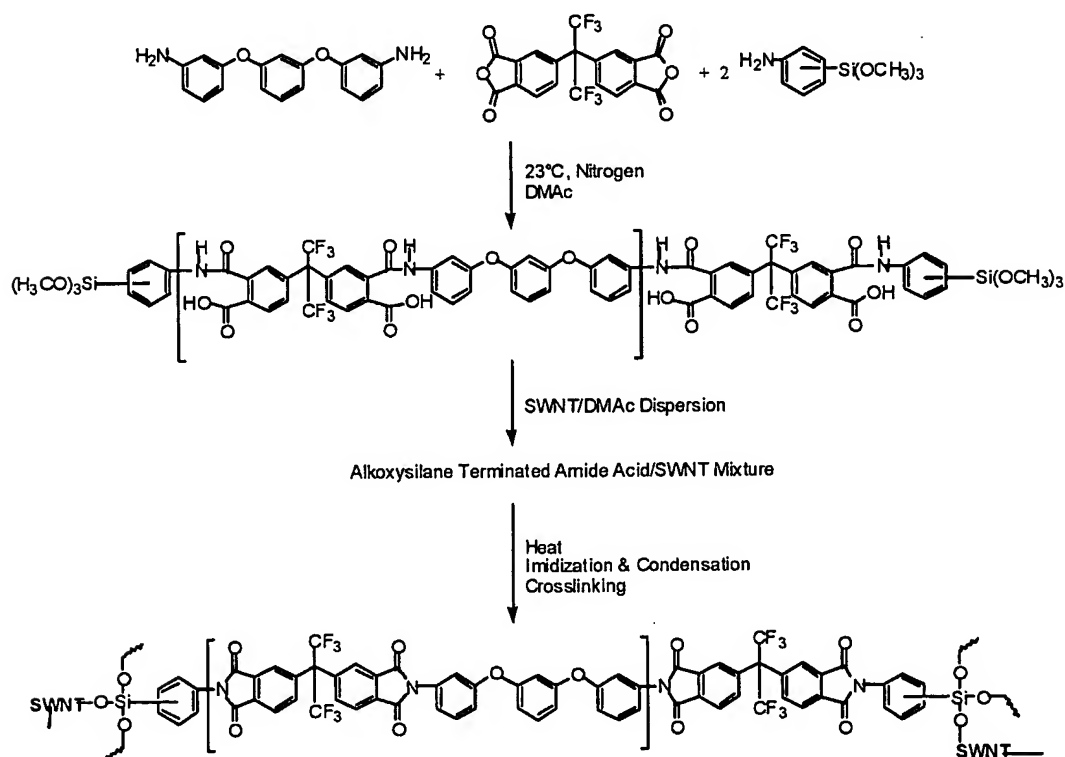


Figure 3. Synthesis of SWNT nanocomposites from Alkoxysilane Terminated Amide Acids

Table 3. Nanocomposite Characterization

SWNT,	T _g ,	Room Temperature Tensile		Elong. @
%	°C	Strength, MPa	Modulus, GPa	Break, %
0	207	131.0	3.73	4.8
0.03	205	122.1	3.54	5.1
0.05	203	138.9	3.72	5.6
0.08	206	136.6	3.77	5.2
HMW*	209	117.2	2.90	----

* High molecular weight, unendcapped version of LaRC™ CP2

material endcapped with alkoxysilane groups. A negligible difference in the T_g of the nanocomposite and HMW, unendcapped materials was observed. A similar effect was observed for the LA SWNT based nanocomposites prepared at a \bar{M}_n of 5000 g/mol; however, the T_gs were greater than that for the HMW material (~213 vs. 209 °C) as expected (9). The tensile properties of the neat polyimide film of the ASTAA containing no SWNTs were greater than that obtained for the HMW version as expected due to the crosslinking provided by the alkoxysilane termination. In general, little effect upon the tensile properties by the incorporation of SWNTs was observed relative to that of the neat ASTAA based film. However, the film containing a 0.03% concentration SWNT exhibited a slight decrease in both the tensile strength and modulus.

Optical transparency at 500 nm and thermo-optical properties were determined and reported in Table 4. The % transmission at 500 nm for the neat ASTAA and HMW, unendcapped versions were comparable, however, the film thickness of the HMW was ~4X that of the neat material. Thus a true comparison can not be made. The film thickness for the ASTAA based materials ranged from 38 to 41 µm. As expected, the % transmission at 500 nm for the nanocomposites decreased with increasing SWNT concentration. The HiPCO SWNT provided darker films as compared to the LA SWNT. For comparison, a 0.1% LA SWNT containing nanocomposite film

Table 4. Optical and Thermo-optical Properties of Nanocomposites

SWNT,	Film	Transmission	Solar	Thermal
%	Thickness, µm	@ 500 nm, %	absorptivity, α	Emissivity, ϵ
0	38	86	0.07	0.59
0.03	38	67	0.21	0.63
0.05	41	59	0.30	0.65
0.08	38	53	0.35	0.67
HMW	127	89	0.07	0.57

prepared from a LaRCTTM CP2 based ASTAA exhibited a 58% transmission for a 71 μ m thick film (9). The % transmission for the neat material prepared at a \overline{M}_n of 5000 g/mol was 84% for a 61 μ m thick film. These results were opposite from those obtained with films prepared from the in-situ polymerization method described above where the LA SWNT provided films with a lower % transmission at 500 nm than the HiPCO based materials. As expected, SWNT incorporation increased the α and ϵ of the films relative to the material prepared from the neat ASTAA solution.

3.4 Conductivity Determination of electrical conductivity is currently underway with the results presented at the conference. The nanocomposite films are anticipated to have sufficient conductivity for static charge mitigation based on previous work.

4. SUMMARY

Nanocomposites were prepared by two different methods from low color polyimides (LaRCTTM CP2 and TOR-NC) and HiPCO SWNTs. By the in-situ polymerization method and alkoxysilane terminated amide acid approach, the nanocomposite films exhibited comparable T_{gs} and room temperature mechanical properties as compared to the neat materials. As the SWNT concentration increased, the optical and thermo-optical properties decreased by both methods with a more marked decrease being observed for the alkoxysilane terminated amide acid approach. HiPCO SWNT containing films exhibited a more marked decrease in optical and thermo-optical properties as compared to LA SWNT containing films prepared at a similar concentration.

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The use of trade names of manufacturers does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

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7. Biographies

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